Particulate Hot Gas Stream Cleanup Technical Issues

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Introduction

The characteristics of entrained particles generated by advanced coal conversion technologies and the harsh flue gas environments from which these particles must be removed challenge current ceramic barrier filtration systems. Measurements have shown that the size distribution, morphology, and chemical composition of particles generated by pressurized fluidized-bed combustion (PFBC) and gasification processes differ significantly from the corresponding characteristics of conventional pulverized-coal ash particles. The entrained particulate matter from these advanced conversion technologies often comprise fine size distributions, irregular particle morphologies, high specific surface areas, and significant proportions of added sorbent material. These characteristics can create high ash cohesivity and high pressure losses through the filter cakes. In addition, the distributions of chemical constituents among the collected particles provide local, highly concentrated chemical species that promote reactions between adjacent particles that ultimately cause strong, nodular deposits to form in the filter vessel. These deposits can lead directly to bridging and filter element failure.

Project Description

This project is designed to address aspects of filter operation that are apparently linked to the characteristics of the collected ash or the performance of the ceramic barrier filter elements. The activities conducted under Task 1, Assessment of Ash Characteristics, are discussed in this paper. Activities conducted under Task 2, Testing and Failure Analysis of Ceramic Filters, are discussed in a separate paper included in the proceedings of the Advanced Coal-Based Power and Environmental Systems '97 Conference. The specific objectives of Task 1 include the generation of a data base of the key characteristics of Hot Gas Stream Cleanup (HGCU) ashes collected from operating advanced particle filters (APFs) and the identification of relationships between HGCU ash properties and the operation and performance of APFs.

During the past year, particulate samples have been characterized from the DOE/FETC Modular Gas Cleanup Rig (MGCR), the Transport Reactor Demonstration Unit (TRDU) located at the University of North Dakota Energy and Environmental Research Center (UNDEERC), the Power Systems Development Facility (PSDF), and gasification studies conducted by Herman Research Pty. Ltd. (HRL) of Melbourne, Australia. This paper discusses these analyses and also presents a coherent mechanism describing how and why consolidated ash deposits form in PFBC filter vessels. This description is based on site observations made at the Tidd PFBC, field and laboratory analyses of ashes and nodules collected

from Grimethorpe, Tidd and Karhula, and a review of literature describing eutectic formation, sintering, and consolidation of boiler tube deposits.

Results

The samples discussed in this paper are briefly described in Table 1. The results of the various physical and chemical analyses performed on these samples are presented in Tables 2 and 3.

Table 1
Identification of Particulate Samples

ID #	Source	Brief description
4198	DOE/FETC MGCR	air-blown fluidized-bed gasifier hopper (10/96)
4199	UNDEERC TRDU	PO50 filter vessel hopper ash (1/14/97)
4195	HRL	Mulgrave test rig: Morwell coal
4196	HRL	Mulgrave test rig: Loy Yang coal
4197	HRL	Mulgrave test rig: Yallourn coal
4231	PSDF	filter cake ash (4/9/97)

Table 2
Physical Characteristics of MGCR, TRDU, HRL and PSDF Particulate Samples

quantity ID #	4198	4199	4195	4196	4197	4231
specific surface area, m^2/g	615	105.3	491	560	429	3.80
Stokes' MMD, μm	0.76	2.4	7.3	3.6	7.2	4.7
uncompacted bulk porosity, %	97	89	87	88	90	85
filter cake porosity, %	--	--	--	--	--	87
drag-equivalent diameter, μm	0.12	2.22	0.906	0.774	0.709	2.05
specific gas-flow resistance, in $H_2O \cdot min \cdot ft/lb$*	9.0	8.5	12.2	10.7	8.4	2.6
true particle density, g/cm^3	2.66	2.26	1.91	1.96	1.98	2.61

  * specific gas-flow resistances were calculated for filter cake porosities equal to the uncompacted bulk porosity of the sample

Table 3
Chemical Characteristics of MGCR, TRDU, HRL and PSDF Particulate Samples, % wt.*

constituent ID #	4198	4199	4195	4196	4197	4231
Li_2O	0.02	0.01	0.08	0.11	0.13	0.027
Na_2O	0.62	0.90	1.4	5.8	1.4	0.52
K_2O	0.15	0.18	0.31	1.3	0.36	1.73
MgO	8.7	11.0	20.9	21.3	22.3	2.12
CaO	24.8	44.0	38.8	16.0	16.9	4.49
Fe_2O_3	2.5	9.0	15.1	11.7	39.3	5.10
Al_2O_3	18.4	15.1	6.2	15.0	5.1	21.89
SiO_2	39.3	12.9	2.9	14.6	1.9	57.25
TiO_2	1.7	1.7	0.22	1.9	0.45	1.15
P_2O_5	0.59	1.0	0.11	0.15	0.22	0.32
SO_3	0.58	1.9	11.1	14.0	12.7	2.53
LOI	32.0	54.2	88.3	93.8	89.5	7.80
soluble $SO_4^=$	< 0.37	0.98	0.65	< 0.47	0.43	--
equilibrium pH*	9.3	10.87	10.2	9.4	9.8	--

* equilibrium pH is dimensionless.

DOE/FETC Modular Gas Cleanup Rig

A site visit was made to the DOE/FETC-MGN MGCR facility in October, 1996 to observe, document and characterize the filter cakes present on the candle filter elements when the filter vessel was opened for refitting. All four candle filter elements were covered with nearly uniform thin cakes. The thickness of the filter cakes on candles A, B, and D was about 0.76 mm, and the thickness of the filter cake on candle C was about 0.51 mm. Using a core sampler to isolate regions of the cake, porosity values of 94.2 and 95.3 % were measured for the filter cake on candle A. The same method applied to the filter cake on candle C yielded values of 94.6 and 94.9 %. Filter cake porosity was also measured by impregnating weighed filter cake nodules from Candle B with ethanol. Five porosity measurements using this technique gave results from 90.8 to 91.8 %. It is not certain whether the actual porosity of the filter cakes on all four candles is closer to 91 or 95 % since the thinness and fragility of the cake challenged both methods.

The remainder of analyses on the MGCR particulate were performed on a hopper sample (ID # 4198) obtained from the same test run. (Although differences due to gravitational settling can exist between filter cake samples and hopper samples this should not be the case with the MGCR samples because of the extreme fineness of this particulate.) The most striking features of this MGCR sample (see Table 2) are its extremely high specific surface area, fine size distribution, and its high uncompacted bulk porosity.

UNDEERC Transport Reactor Development Unit

A sample of particulate collected in the TRDU hopper during a recent gasification run comprises relatively fine, black particles. This sample has a relatively high uncompacted bulk porosity, a high

specific surface area, and a small drag-equivalent diameter (Table 2). The specific gas-flow resistance of this sample is not abnormally high.

Herman Research Pty Ltd.

The HRL samples were collected from the hot gas filter in the pressurized gasification test rig at Mulgrave, Australia during testing with three different Latrobe Valley brown coals. Gasification was carried out at about 900 kPa and about 900 °C. Although the filter was operated at this same pressure, the temperature in the filter was around 400 °C. These samples have similar physical characteristics. They all exhibit extremely high specific surface areas, and moderate drag-equivalent diameters and uncompacted bulk porosities (for gasification samples). Although the values of specific gas-flow resistance measured for these samples are relatively high, filtering pressure drops should be manageable with these samples.

General Characteristics of Gasification Particulates

Overall, the characteristics of the gasification samples from the MGCR, TRDU and the HRL Mulgrave test rig are similar to other samples of gasification particulate that have been analyzed previously. The median size of gasification particles from a given facility is dependent on the design of the facility and the specific operation of the gasification process. The typical characteristics of gasification particulates include irregular particle shapes, high specific surface areas, and relatively high values of uncompacted bulk porosity and specific gas-flow resistance. Filter cakes comprising gasification particulates must maintain relatively porous structures to prevent excessive filtering pressure losses. If these filter cakes compact or consolidate significantly, the effect of the high specific surface area of the particles on pressure drop could be severe. As operating experience with gasification facilities accumulates, the structure of filter cake samples from these facilities will be studied to determine if factors such as differential pressure drop across the cake or exposure time tend to alter the structure of the cake.

Because the relationships between chemical constituents and particulate behavior are not established for gasification particulate, the effect on filtration behavior of the various chemical compounds present in gasification particulate samples are not yet known. Chemical reactions such as tar formation and chemical sintering between particles have the potential to create serious problems such as bridging in filters collecting gasification particulates.

Power Systems Development Facility

A site visit was made to the PSDF in April, 1997 to observe, document and characterize the filter cakes present on the candle filter elements and other filter vessel deposits when the filter vessel was opened for refitting after a period of operation in combustion mode. All of the candle filter elements were covered with patchy, thin cakes. The thickness of the filter cakes ranged from about 0.1 to 1 mm. (Because the filter was extensively pulse-cleaned prior to shutdown, the thickness of these cakes does not necessarily represent the condition of the cakes during operation.) Filter cake porosity was measured for nodules from the PSDF filter cake by impregnating weighed filter cake nodules with ethanol. This method yielded an average porosity of 87 %. The bulk PSDF ash sample collected during the site visit (ID # 4231) exhibited a range of beneficial characteristics: low specific surface area, moderate particle size and

uncompacted bulk porosity, a relatively large drag-equivalent diameter, and a low specific gas-flow resistance. However, because operation of the PSDF combustor is still in its early stages, the characteristics of PSDF ashes produced in later operation must continue to be monitored.

**Mechanism Describing the Consolidation of Ash Deposits in PFBC Filters**

Figure 1 presents SEM photographs of fresh fracture surfaces of filter cake nodules taken from the filters at Tidd and Karhula which demonstrate that the nodules found in these filters are concretions composed of discrete fine particles almost completely embedded in pervasive amorphous masses. These masses apparently form in the filter vessel after the particles are initially collected. The appearance of these nodules, in combination with other laboratory analyses of ash deposits from Grimethorpe, Tidd, and Karhula, and a review of the effects of ash chemistry on particle bonding has allowed the development of the following description of the mechanism responsible for the consolidation of ash deposits in PFBC filter vessels.

The formation of strong, consolidated ash deposits begins with direct contacts between collected particles comprising highly concentrated, dissimilar chemical compounds. Chemical species exist in high local concentrations in particles collected in HGCU filters applied to PFBC processes because of the nature of the process. In conventional pulverized coal combustion, the fly ash particles are generated through carbon burnout, melting, or vaporization/condensation processes. These latter two mechanisms produce individual ash particles containing a broad array of chemical compounds. In the PFBC process, the coal and sorbent particles introduced into the combustor are never exposed to high enough temperatures to undergo either significant rapid melting, or vaporization and condensation. The chemical compositions of the entrained particles that leave the boiler result from either carbon burnout around mineral inclusions in the coal, or carryover of alkaline sorbent particles that have been mostly sulfated in the combustor. Therefore the individual particles entering the HGCU filter are much more likely to be predominantly composed of a single compound. Distinct chemical compositions of various individual particles found in ash deposits obtained from the Tidd APF have been observed with SEM microprobe analyses [1]. Consequently the ash deposits in a PFBC HGCU filter contain a high proportion of intimate interparticle contacts between highly concentrated, distinct chemical compounds.

Although HGCU temperatures are not high enough to melt these concentrated compounds, solid-to-solid diffusion gradually occurs between dissimilar compounds in direct contact. The formation of interparticle melts resulting from these direct contacts is shown generically in Figure 2. As the compounds diffuse together in the region of particle contact, compositions are eventually obtained that begin to melt at the HGCU operating temperature. (The points corresponding to these compositions are labeled C_1 and C_2 in Figure 2.) The interparticle melts that form act as fluxing agents, speeding the diffusion of chemical species into the region of interparticle contact. Eventually, the composition of the interparticle melt reaches the eutectic composition, which is established by minimizing the overall system energy for the combination of compounds involved in the process. The eutectic composition is the particular combination of the compounds that yields the minimum melting point. The melting point of the eutectic is lower, often by a significant amount, than the melting points of any of the chemical compounds contained in the eutectic composition.
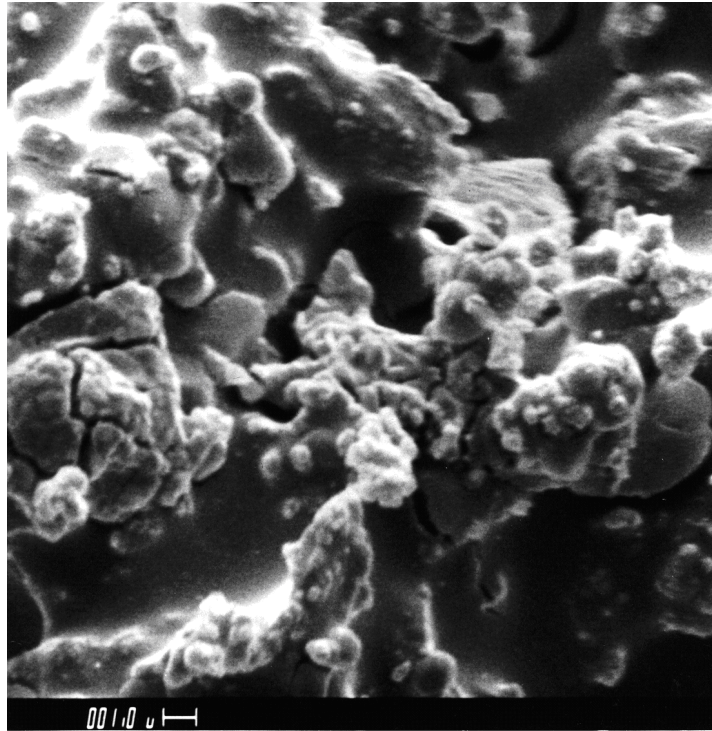
(a)
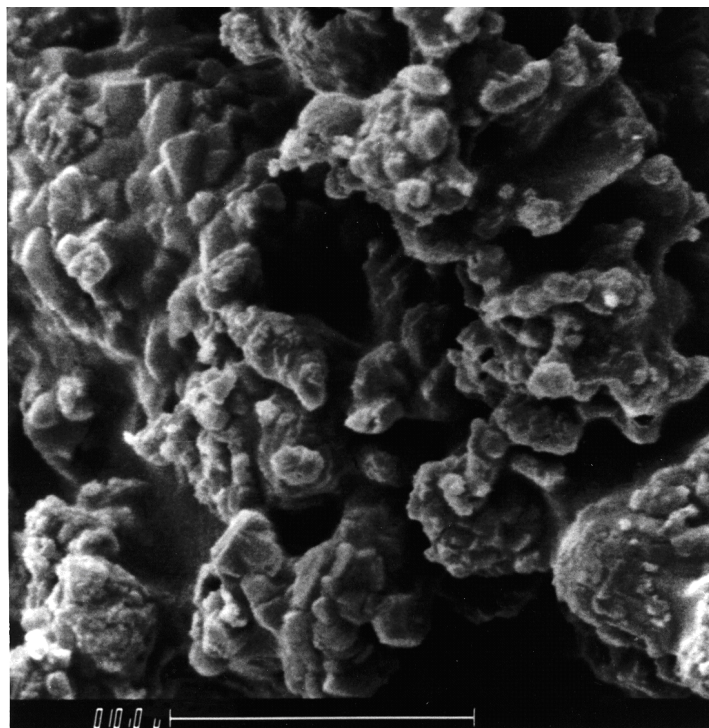
(b)

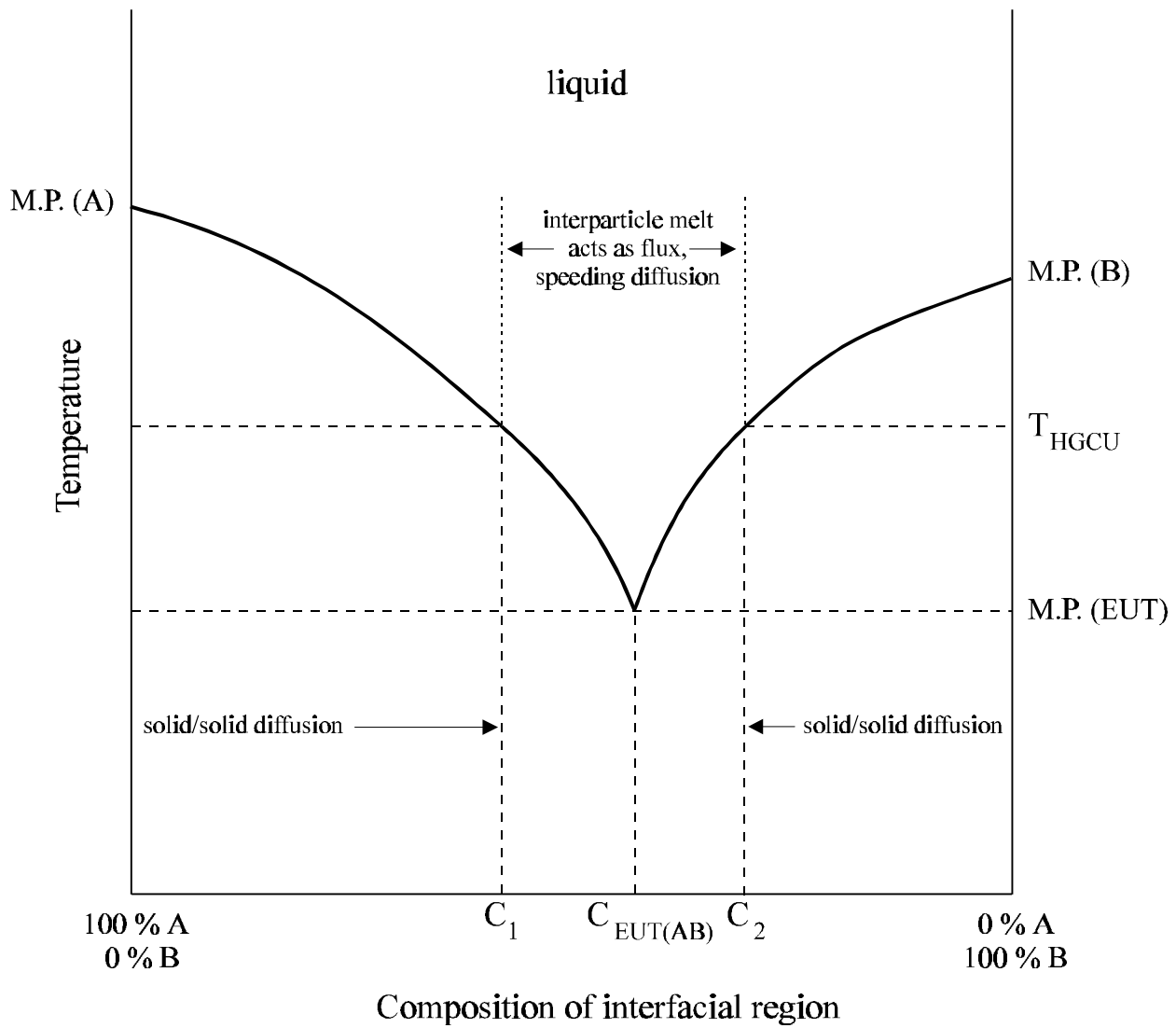Figure 1. SEM photographs of fresh fracture surfaces of filter cake nodules taken from a) Tidd and b) Karhula.

Figure 2. Binary phase diagram showing the formation of a eutectic (AB) resulting from surface diffusion between solid compounds A and B in contact. Eutectic (AB) has a melting point < the temperature of the HGCU filter. Compositions C_1 and C_2 have melting points equal to the temperature of the HGCU filter.

Therefore, any adjacent particles that place two distinct compounds in direct contact will tend toward the formation of a eutectic at the interparticle contact point. The rate at which the eutectic composition is approached is determined by several factors. These include the purity of the component compounds, the geometry of the interparticle contact (particle size and contact area), the pressure of contact between the particles, the temperature of the particles, and the fluxing action of intermediate compositions of the component compounds. In addition, other factors that exist in HGCU filters may also influence the rate of eutectic formation. These include the presence of gaseous compounds in the pressurized flue gas surrounding the particles, and additional compounds that are probably present in relatively low concentrations in the contacting particles. (In general, the melting point of a eutectic will be further decreased by the addition of more chemical species into the eventual eutectic composition.)

Based on the nature of the PFBC process and the measured bulk compositions (see Table 3) of various ash samples obtained from APFs at PFBC facilities, there are several compounds that are likely to be available in PFBC ash deposits. Some of the compounds that may be found in high concentrations in individual PFBC ash particles include K_2SO_4, $CaSO_4$, $MgSO_4$, Na_2SO_4, K_2O, MgO, SiO_2, Al_2O_3, and Fe_2O_3. A review of multicomponent system phase diagrams involving combinations of these compounds was conducted. Table 4 lists systems (combinations of compounds) with eutectic compositions that melt below 1600 °F and their eutectic melting points. It is evident from the melting points in Table 4 that APFs collecting PFBC ash and operating at or near 1600 °F probably provide the conditions necessary for the development of melts at many of the interparticle contact points in the various ash deposits formed in the filter. Given enough time, these interparticle melts will develop.

Table 4
Systems Containing Compounds that can Combine and Melt Below 1600 °F [2]

| System	Relative Amounts, % wt.	Melting Point, °F
K_2SO_4 - $CaSO_4$ - $MgSO_4$	70-5-25	1346
K_2SO_4 - $MgSO_4$	72-28	1382
K_2SO_4 - Na_2SO_4	21-79	1513
SiO_2 - K_2O - Na_2O	69-23-8	1004
K_2SO_4 - Na_2SO_4 - $MgSO_4$	15-55-30	1193
$CaSO_4$ - Na_2SO_4 - $MgSO_4$	5-59-36	1202
MgO - Na_2O	63-8-29	1315
K_2O - SiO_2	33-67	1382

As the volume of an interparticle melt grows, the surface capillary force exerted by the surface tension of the liquid melt gradually rearranges the collected particles into a more compact structure. This effect is shown schematically in Figure 3. In addition to the detrimental effects this consolidation (reduction in the porosity of the deposit) has on filtering pressure losses, the interparticle bonding forces increase, causing the overall deposit to have significantly greater strength.

Because the environment in which a PFBC ash deposit is present in an APF includes all the ingredients necessary to form these detrimental, consolidated deposits, it is important to consider all the factors that
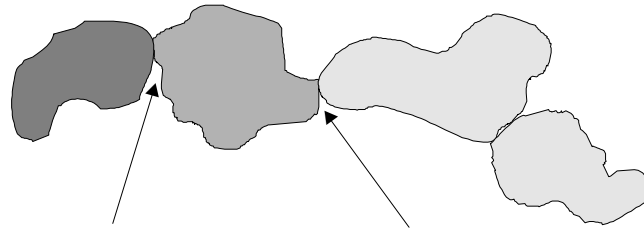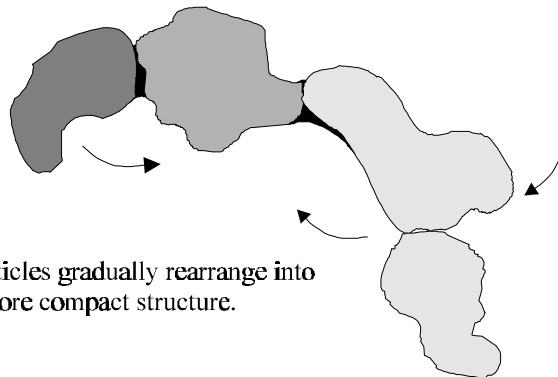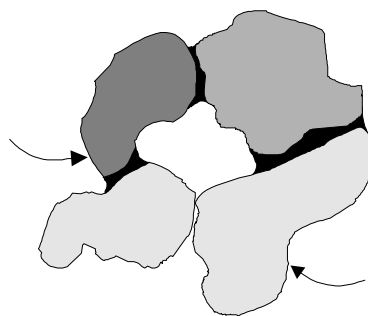
Diffusion of solid compounds occurs at contacts
between particles of dissimilar composition.
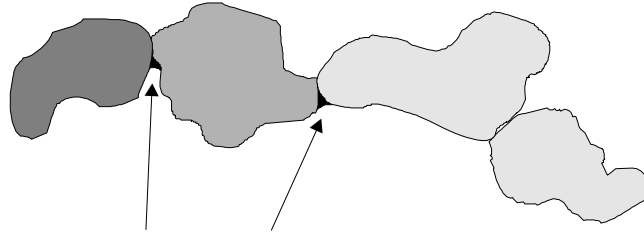
Diffused compounds form interparticle melts.
These melts act as flux, increasing the rate of diffusion.
The surface tension of interparticle melts begins to rearrange particle contacts.

Particles gradually rearrange into
a more compact structure.

The deposit consolidates. Eutectic melts fill much of the interstitial volume.
Particle bonds strengthen.

Figure 3. Schematic representation of the consolidation of ash deposits.

influence the rate at which these deposits will consolidate. The consolidating force, which results from the development of interparticle melts between adjacent particles, is dependent on the particle size, the viscosity and surface tension of the interparticle melt, as well as the time of exposure of the particles to the forces exerted by the surface tension of the melt [3,4]. The size distribution of the particles in the ash deposit is controlled by the parameters of the PFBC process, the characteristics of the coal and sorbent, and the design of the particle filter (and any inertial collectors, if they are included in the collection system). The viscosity and surface tension of the melt are functions of the chemical composition of the melt, and the HGCU temperature [4]. Figure 4 shows the dependence of the dimension of the interparticle melt on particle size [4]. Figure 5 demonstrates that if given sufficient time, even an interparticle melt that is highly viscous at HGCU conditions will eventually cause the formation of particle bonds with significant size [4]. It is evident from these data and the nature of the mechanism governing the formation of consolidated ash deposits in PFBC filters that the time that the collected ash particles are allowed to reside in the APF must be minimized.

Future Activities

There are also reasons to believe that portions of the mechanism describing deposit consolidation may apply to deposits of gasification particulate, although experimental verification must be carried out on appropriate samples collected from filters applied to this process. Laboratory analyses are also planned to further verify and characterize this mechanism, as well as to specifically identify the compounds that are involved in the formation of interparticle melts. One ultimate goal of this type of investigation may be the pursuit of some means of preventing ash deposits that do remain in filter vessels for long periods of time from undergoing this consolidation. However, give the nature of the consolidation mechanism, it is possible that the only feasible solution to this problem will be to limit time of exposure of ash deposits to the elevated temperatures found in the APF.
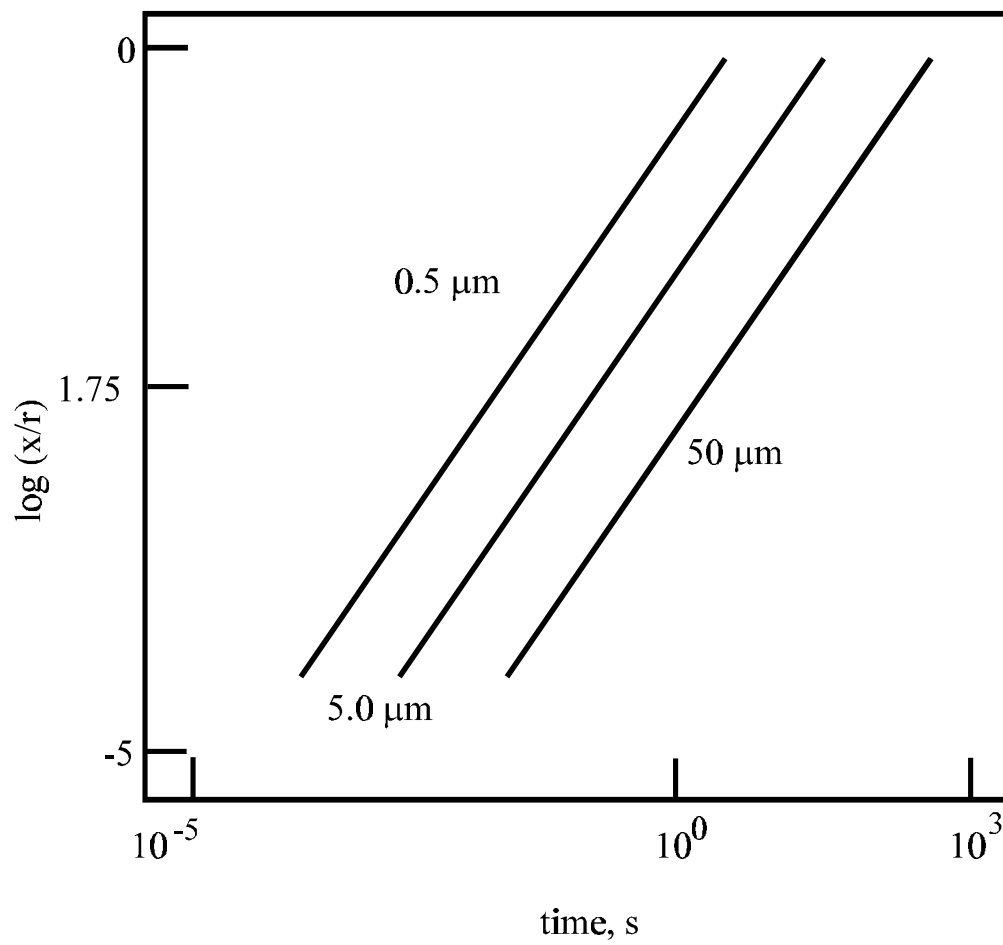
Acknowledgments

Figure 4. Sintering as a function of time for a range of particle sizes.
Sintering is expressed as x/r, where x = radius of the interparticle interface,
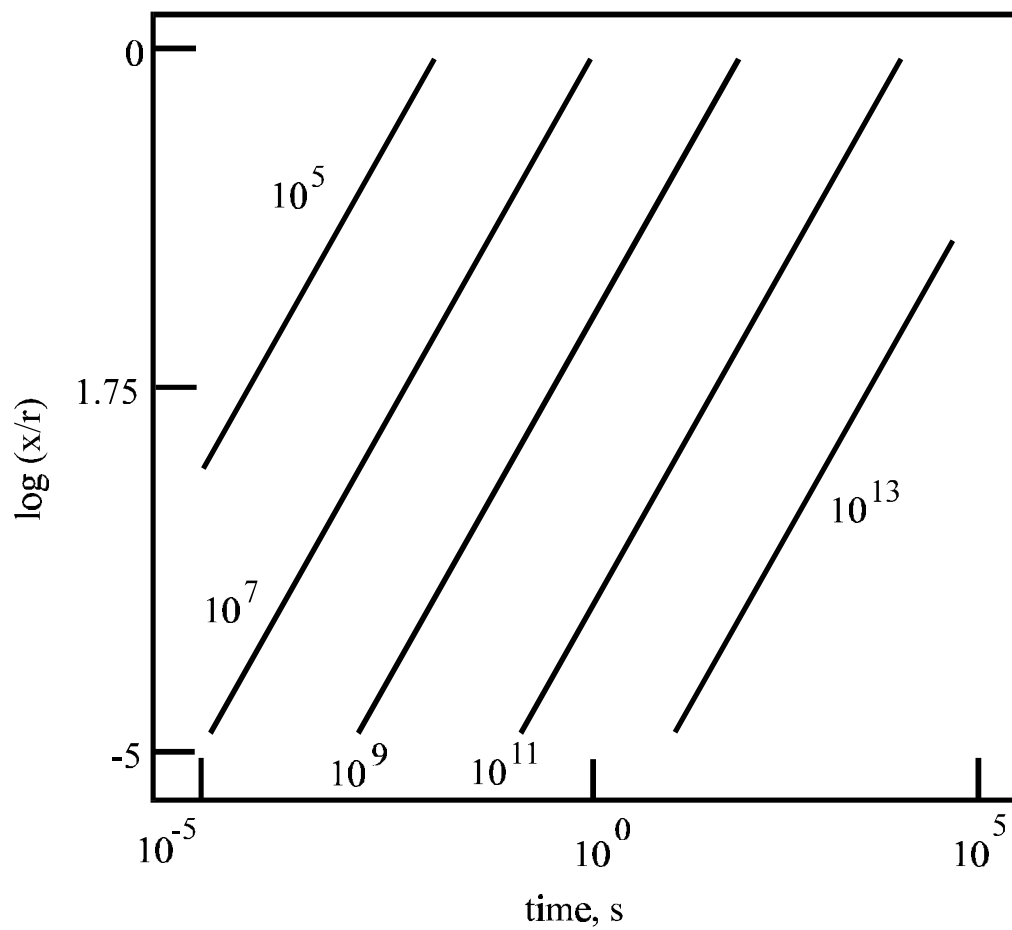and r = the particle radius.

Figure 5. Sintering as a function of time for a range of viscosities. Sintering is expressed as x/r, where x = radius of the interparticle interface, and r = the particle radius. Values of viscosity are given in poise.

References

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